

RESID CONVERSIONS WITH CATALYSTS DERIVED FROM PHOSPHOMOLYBDATES

Belma Demirel, Ann Thomas and Edwin N. Givens

University of Kentucky Center for Applied Energy Research, 2540 Research Park Drive,
Lexington, KY 40511-8410

ABSTRACT

Hydroconversion of coal and petroleum derived heavy resids have been studied using both dispersed and impregnated Mo catalysts derived from phosphomolybdic acid (PMA). The dispersed catalysts were generated *in situ* by introducing the PMA supported on coal. During reaction the support essentially disappears producing a highly dispersed Mo catalyst, which is as active as the catalysts produced from common organic-soluble Mo precursors. The activity of PMA impregnated high-surface area aluminas has been compared with commercially available Mo catalysts. The resid conversion activities of catalysts prepared from both Ni and Co phosphomolybdates have also been determined. The activities of the alumina supported salts will be compared with the corresponding commercially-available alumina-supported bimetallic catalysts.

INTRODUCTION

Resid is defined as the fraction of petroleum, bitumen or coal liquids that does not distill under vacuum at atmospheric equivalent boiling points over 500°C. Resids are typically coked, hydroprocessed or used in manufacturing asphalts [1-5]. Coprocessing of coals with petroleum resid has been the subject of a number of studies in recent years with the intention of integrating coal into conventional petroleum refining operations [2, 3, 6-10]. Studies have suggested that combining coal liquefaction and heavy residue upgrading is economically feasible. It has been claimed that the presence of coal will reduce the deposition of coke and metals on the catalyst. In addition, heavy resids will also act as hydrogen transfer agents for coal conversion [2-4, 11-12].

In the near future, the resid content is expected to increase as price increases. Therefore, it becomes necessary to upgrade these fractions into distillable fractions. Hydrogenation is required in order to convert resids into more valuable products. Molybdenum based catalysts are generated *in-situ* from inorganic or organometallic compounds as precursors [13]. The metal precursors typically decompose thermally transforming into highly dispersed metal sulfides [14]. Although the exact form of the catalyst is not known, it appears to be some form of molybdenum sulfide, although apparently not MoS₂. Lopez et al. reported that the atomic ratio of molybdenum was less than two in the active catalysts isolated from processing heavy petroleum fractions with ammonium molybdate and thiomolybdate precursors [15]. Polyoxomolybdates have been known to create active, well-dispersed catalysts for converting both coal and resids. Bearden and Aldridge [16, 17] and Gatsis and Plaines [18] have reported hydroconversion processes for converting oil, coal or mixtures utilizing a catalyst prepared by first forming an aqueous solution of PMA and phosphoric acid. Our studies showed that phosphomolybdic acid (PMA) is readily transformed in the reaction media to produce an active form of catalyst for liquefaction of Wyodak coal [5, 19].

We have further expanded our work on PMA derived catalysts to investigate various methods of dispersing the molybdenum in the reaction mixture. The use of coal as a carrier is intriguing since it is inexpensive and largely converts to liquid product during the reaction thereby eliminating the necessity of recovering and disposing of a solid byproduct. Unfortunately, coal does not possess the unique activating effect that alumina imparts to molybdenum catalysts. This work reported here compares the activities of precursors when dispersed on coal and supported on Al₂O₃. The objective of this work is to convert both coal and petroleum derived resids to distillates boiling below 525°C using PMA and Ni and Co phosphomolybdate precursors.

EXPERIMENTAL

Wyodak coal from the Black Thunder Mine in Wright, Wyoming was supplied by Hydrocarbon Technologies, Inc. Proximate and ultimate analysis of the coal are given in Table 1. The solvents combined a 343-524°C distillate (Wilsonville Run 258 period B) and 524°C⁺ deashed resid (Wilsonville Run 258 period A) that were obtained from the Advanced Coal Liquefaction R&D

Facility at Wilsonville, Alabama. Alumina was obtained from AKZO (AO-60; surface area, 180 m²/g). Phosphomolybdic acid (PMA) was supplied by Aldrich Chemicals Inc. Co₃(PMo₁₂O₄₀)₂ (CoPM), Ni₃(PMo₁₂O₄₀)₂ (NiPM) and K₃PMo₁₂O₄₀ (KPM) were synthesized in our laboratory.

The Ni, Co and K salts of PMA were impregnated onto either coal or Al₂O₃ by adding aqueous solutions that contained the appropriate concentration of the individual metal salts to provide a final loading of 15 mg or 1000 mg of Mo per kg feed. During addition, the powdered coal or the Al₂O₃ support was continually stirred to assure even dispersion. The potassium salt was soluble only after adding a few drops of KOH to the water.

Activity tests were carried out in a 50-cc micro autoclave at 440°C and 1350 psig (cold) for 30 minutes. The reactor was equipped with a thermocouple, and connected to a pressure transducer for monitoring temperature and pressure during the reaction. Experiments were repeated at least once to confirm the reproducibility. In a typical experiment, 2.5 g of 524°C distillate, 4.0 g of deashed resid and 0.35 g of metal impregnated coal (on dry basis) or Al₂O₃. The reactor was loaded, pressurized with H₂S/H₂ (3 wt% H₂S in H₂), submerged in a fluidized sand bath and agitated continuously at the rate of 400 cycles per minute at the specified temperature. After quenching, solid and liquid products were removed from the reactor using tetrahydrofuran (THF). The filtered solids were extracted in a Soxhlet extractor overnight. The THF insoluble fraction was dried in a vacuum oven and weighed. The soluble fraction was distilled under vacuum (modified ASTM D-1160-87) to an atmospheric equivalent end point of 524°C. Resid conversion was calculated as follows:

$$\text{Resid Conv} = \left(1 - \frac{524^\circ\text{C} \cdot \text{Resid}_{\text{out}}}{524^\circ\text{C} \cdot \text{Resid}_{\text{feed}} (\text{madf})} \right) \times 100$$

where madf is moisture, ash and distillate free. Mayan resid was processed with precursors dispersed or supported on coal or Al₂O₃. Larger scale simulations were performed in a 300-cc autoclave.

RESULTS AND DISCUSSION

PMA is a unique Mo precursor since it is relatively stable even in the presence of hydrogen to temperatures in excess of 300 °C. The stability of PMA has been associated with the Keggin structure in which the 12 Mo atoms surround the central phosphorus atom. The catalytic activity of PMA in a number of oxidation reactions has been associated with the Keggin structure. Although H₂S causes limited sulfidation at somewhat lower temperatures, the limited introduction of sulfur in the structure suggests that some ionic features may still be intact at relatively high temperatures, though certainly not at liquefaction temperatures. Yong et al. recognized that, in some cases, associated cations impart additional thermal stability on the Keggin structure [22]. For this reason, the thermal and catalytic activity of three metallic salts of PMA were investigated, namely the Co, Ni and K, and compared with the activity of PMA.

The thermal stability of the three salts in He is shown in Figure 1. The endotherm associated with dehydration of these materials is quite different for these salts. The K salt appears to dehydrate most rapidly, even more rapidly than PMA. Dehydration of the Ni and Co salts occurs over a much wider temperature range. An endothermic spike appears for these two salts at 330-400 °C which is lower than for PMA. This has been ascribed to the loss of constitutional water and collapse of the Keggin structure. Such a spike is not observed in the K structure until 500 °C suggesting that the Keggin ion may be stable at this temperature. In H₂ (see Figure 2), the initial loss of water from KPM occurs over a more narrow temperature range than for PMA. The material formed at 150 °C is quite stable. By contrast, the Ni salt and, to a lesser extent, the Co salt appear to continually lose weight over the whole region suggesting that dehydration is quickly followed by further changes in the ionic structure. After dehydration, the K salt is unusually stable at temperatures beyond 450 °C suggesting that the Mo may have remained in the +6 oxidation state. When H₂S is added along with H₂ (Figure 3), the PMA and Ni salt show a major loss in weight at approximately 300 °C, probably indicating breakdown of the Keggin ion. The K salt showed initially a weight gain suggesting incorporation of sulfur into the structure. However, at 350 °C, a very significant loss in weight occurs in an exothermic reaction. This suggests formation of a significant amount of water, destruction of the Keggin structure and reduction of Mo, probably to the +4 state, although this has not been confirmed. Clearly, the H₂S leads to a significant change in the stability of the K salt.

Resid conversions in the absence of a catalyst (Table 2) after 30 min was 10.9%. When coal equivalent to the amount used as a carrier for the metal catalyst was added to the reaction mixture, conversion increased by 1%. Although the thermal conversions are still incomplete, they are essentially unaffected by the presence of the coal. The addition of PMA at the 1000 ppm for the 30 min runs increased resid conversion by about 2%, whereas at the 15 ppm level there was no change

(Table 3). Increasing the run time to 90 minutes gave a significant increase in the level of conversion, also for the thermal reaction. Since the 15 ppm metal addition probably had no effect, the 21-22% conversion observed for both PMA and CoPM at this level is probably indicative of the thermal reaction. Increasing the metal concentration to 1000 ppm gave a sizable increase in conversion. Both PMA and the CoPM gave 31% conversion of resid to distillate. Although this work is in progress, it will be used to guide processing runs to be performed in a continuous batch configuration. The results from the conversion of petroleum resids and larger scale simulations will be discussed.

CONCLUSION

Thermal stability tests of PMA and bimetallic phosphomolybdates showed that these materials are mostly stable up to 400-450°C in the presence of He or H₂. The H₂S leads to a significant change in the stability, but transforms these materials into an active form of catalyst. Catalytic activity tests of PMA and bimetallic phosphomolybdates also showed that they have significant effect on resid conversion.

REFERENCES

- [1] Nelson, W. L., *Petroleum Refinery Engineering*, McGraw-Hill, NY, 1958.
- [2] Curtis, C. W., Guin, J. A., Pass, M. C. and Tsai, K-J., *Prepr. Pap.- Amer. Chem. Soc., Div. Fuel Chem.* **1984**, 29 (5), 155.
- [3] Curtis, C. W., Guin, J. A., Pass, M. C. and Tsai, K-J., *Fuel Sci. Technol. Int.* **1987**, 5, 245
- [4] Moschopedis, S. E. and Hepler, L. G., *Fuel Sci. Technol. Int.* **1987**, 5, 1.
- [5] Demirel, B. and Givens, E. N., *Energy and Fuels* (in print).
- [6] Curtis, C. W., Tsai, K-J. and Guin, J. A., *Ind. Eng. Chem. Res* **1987**, 26, 12.
- [7] Curtis, C. W., Tsai, K-J. and Guin, J. A., *Fuel Process. Technol.* **1987**, 16, 71
- [8] Curtis, C. W. and Cassell, F. N., *Energy and Fuels* **1988**, 2, 1.
- [9] Flynn, T., Kemp, W., Steedman, W., Bartle, K. D., Burke, M., Taylor, N. and Wallace, S., *Fuel Process, Technol.* **1989**, 23, 197.
- [10] Steedman, W., Flynn, T., Kemp, W., Bartle, K. D., Taylor, N. and Wallace, S., *Int. J. Energy Research* **1994**, 18, 299.
- [11] Huber, D. A., Lee, Q., Thomas, R. L., Frye, K. and Rudins, G., *Prepr. Pap.- Amer. Chem. Soc., Div. Fuel Chem.* **1986**, 31 (4), 227.
- [12] Gray, M. R., *Upgrading Petroleum Residues and Heavy Oils*, Marcel Dekker, Inc., N.Y., 1994.
- [13] Del Bianco, A., et al., *Appl. Cat. (A)* **1993**, 94, 1.
- [14] Kim, H. et al., *Prepr. Pap.- Amer. Chem. Soc., Div. Fuel Chem.* **1989**, 34, 1431.
- [15] Lopez, J. McKinney, J. D. and Pasek, E. A., U.S. Patent 4557821, Dec. 10, 1985.
- [16] Bearden, R. and Aldridge, C. L., U. S. Patent 4,637,870, Jan. 20 1987.
- [17] Aldridge, C. L. and Bearden, R., U. S. Patent 4196072, Apr. 1, 1980
- [18] Gatsis, J. G. and Plaines, D., U. S. Patent 3331769, July 18, 1967.
- [19] Demirel, B. and Givens, E. N., *Catalysis Today* (in print)
- [20] Del Bianco, A., Panariti, N., Anelli, M., Beltrame, P. L. and Carniti, P., *Fuel* **1993**, 72, 75.
- [21] Marchionna, M., Lami, M. and Ancillotti, F., *Fuel Process. Technol.* **1994**, 40, 1.
- [22] Yong, W. J., Quan, X. X. and Zheng, J. T., *Thermochemica Acta* **1987**, 111, 325.

ACKNOWLEDGEMENT

The authors gratefully acknowledge financial support provided by the U.S. Department of Energy Federal Energy Technology Center under contract number DE-AC22-91PC91040.

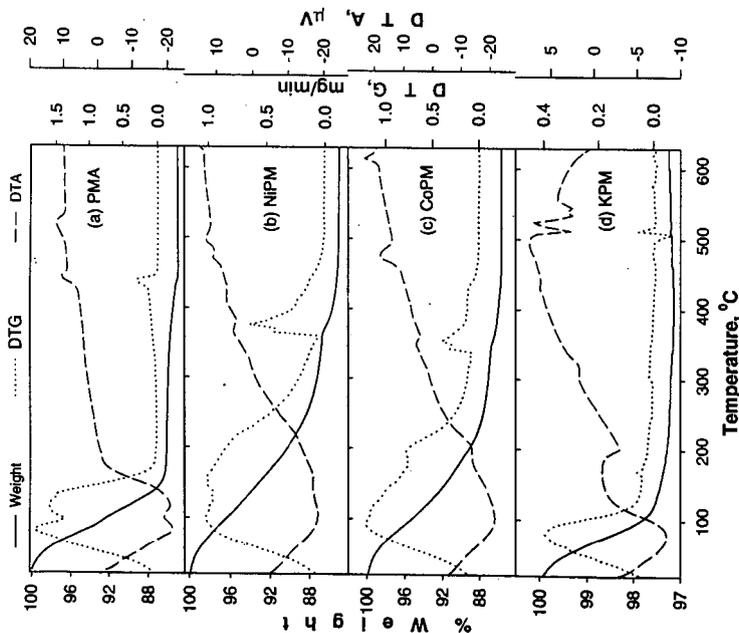


Figure 1. TG spectra of PMA and bimetallic phosphomolybdates in He.

Table 1. Analysis of Wyodak Black Thunder Coal.

Proximate Analysis		w%	Ultimate Analysis		w%(dry)	Sulfur Analysis		w%
Moisture		8.89	Carbon		70.62	Total		1.94
Ash		5.76	Hydrogen		5.03	Pyritic		0.80
Volatile matter		39.88	Nitrogen		1.13	Sulfate		0.80
Fixed carbon		45.47	Sulfur		0.52	Organic		0.34
			Oxygen (diff)		16.38			
			Ash		6.32			
			Ash, SO ₂ -free		5.47			

Table 3. Conversion of coal resid using PMA and CoPM.

Precursor	Resid Conversion, wt%			
	PMA		CoPM	
Reaction time, min	30	90	30	90
15 ppm Mo/g feed	11.9	22.2	12	21.1
1000 ppm Mo/g feed	14.3	31.2	--	31.4

Table 2. Conversion of coal resid without catalyst.

Reaction time, min	Resid conversion, wt%	
	30	90
no catalyst, with coal	10.9	--
no catalyst, no coal	11.9	--

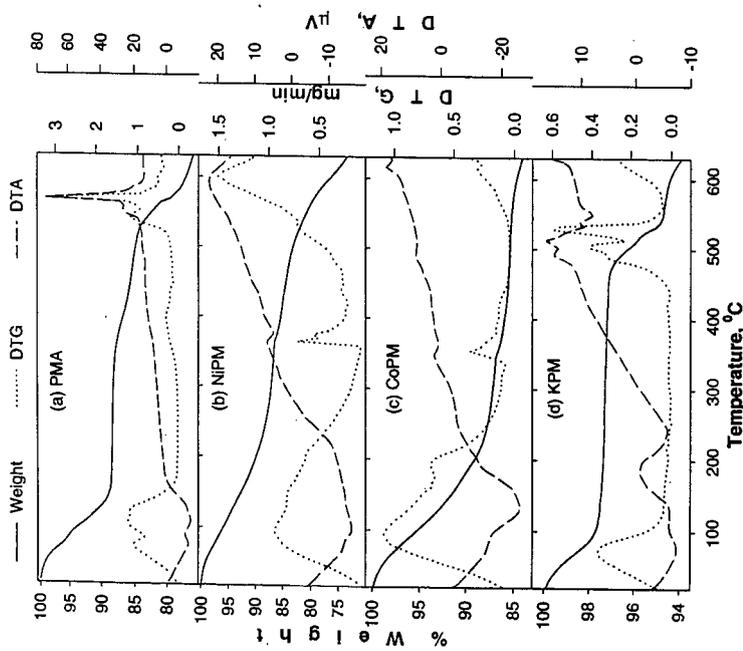


Figure 2. TG spectra of PMA and bimetallic phosphomolybdates in H_2 .

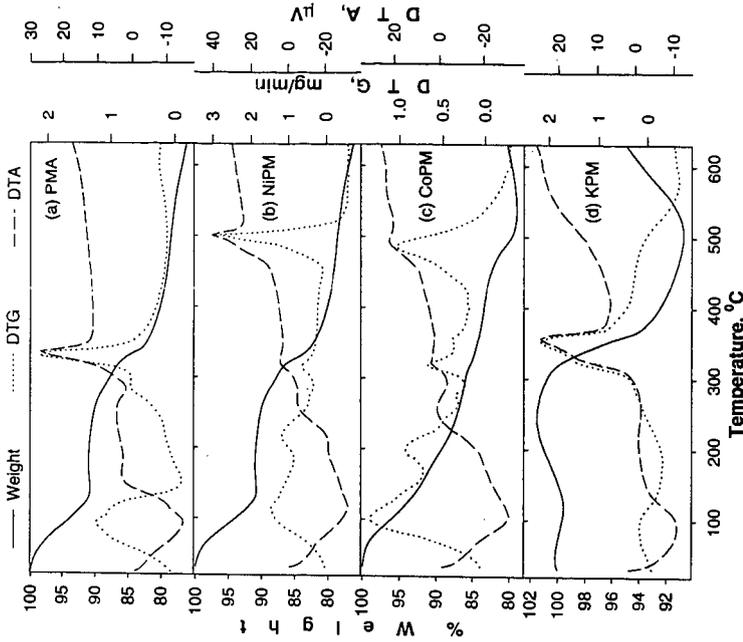


Figure 3. TG spectra of PMA and bimetallic phosphomolybdates in H_2S/H_2 .